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# Identification and classification of components in flash pyrolysis oil and hydrodeoxygenated oils by two-dimensional gas chromatography and time-of-flight mass spectrometry

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**Abstract**

Hydrodeoxygenated pyrolysis oils (HDO) are considered promising renewable liquid energy carriers. To gain insights in the various reaction pathways taking place during the hydrodeoxygenation reaction of pyrolysis oil, two-dimensional gas chromatography with time-of-flight mass spectrometric analyses (2D-GC–TOF-MS) was applied on the feedstock and product oil. Chromatographic parameters like injection temperature and column choice of the $^{1}$D-$^{2}$D ensemble are discussed. Fractionation of the oils by hexane extraction was applied to show the distribution of analytes over the phases. Some 1000 and 2000 components in the pyrolysis and HDO oil, respectively could be identified and classified. The TOF-MS detection considerably improved the understanding of the molecular distribution over the $^{1}$D-$^{2}$D retention time fields in the contour plot, in order to classify the analytes in functional groups. By group-type classification of the main components (>0.3% relative area), it was possible to characterize the oils by 250 and 350 analytes, respectively pyrolysis oil and HDO oil, describing 75% of the chromatographable fraction. The 2D-GC–TOF-MS method showed to be a useful and fast technique to determine the composition of (upgraded) pyrolysis oil and is potentially a very useful tool for exploratory catalyst research and kinetic studies. The 2D-GC–TOF-MS technique is not only useful for the chemical study as such, but also provides the basic knowledge for method transfer to a 2D-GC-FID (flame ionization detector) application.


*Keywords:* Comprehensive two-dimensional GC; Time-of-flight TOF mass spectrometry; Flash pyrolysis oil; Hydrodeoxygenated HDO oil; Fractionation; Identification and classification of components; Kinetic and catalyst study

## 1. Introduction

Flash or fast pyrolysis of biomass is considered a promising technique to produce environmentally friendly liquid energy carriers [1]. As such, it cannot be applied in in-stationary combustion engines and upgrading is required. An interesting upgrading reaction is hydrodeoxyenation, in which the pyrolyis oil is treated with hydrogen using heterogeneous catalysts [2].

Pyrolysis oil is a complex mixture of a broad range of organics belonging to different product groups (alcohols, acids, aldehydes, phenolics, sugars). The complex composition of pyrolysis oil is due to the large number of reactions taking place when pyrolysing the main components of the biomass-feedstock (cellulose, hemicellulose and lignin). To gain insights in the molecular composition of pyrolysis oil, fractionation schemes using liquid–liquid extraction have been developed, followed by instrumental separation and detection techniques like GC, GC-MS, liquid and gel permeation chromatography (LC and GPC) and Fourier transform infra red spectroscopy (FTIR) [3–5]. Using these fractionation techniques, the pyrolysis oil is characterized by an apolar fraction (hydrocarbons, aromatics) a polar fraction (sugars, acids, phenolics) and an insoluble lignin fraction. GC–MS analysis of pyrolytic oils and their fractions to identify the major components was already reported by Polk and Phingbodhipakkiya [6] in 1980. To simplify sample pre-treatment, separation of the phenolic fraction by GPC was applied by Andersson et al. [7]. By a subsequent LC–LC separation of the phenolic fraction repeatable and reliable quantitative results for some 10 phenolic derivatives were obtained.

A composition analysis by combination of several chromatographic techniques after fractionation of biomass-based flash pyrolysis oils was published by Desbène et al. [8] and Oasmaa et al. [9]. A direct analysis technique of pyrolysates by

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a combination of electrospray-assisted pyrolyis ionisation and mass spectrometry during Curie-Point pyrolysis was described by Hsu et al. [10]. The gaseous pyrolysates were directly injected in an ionization source of the mass spectrometer, without chromatographic separation. By selective ionization (trace) amounts of polar pyrolysates could be detected in the presence of large quantities of non-polar hydrocarbons. Schnitzer et al. [11] have been using a soft field ionisation mass spectrometric (FIMS) technique for the characterization of pyrolysates from manure, bio-oils and char. They were also able to identify intact pyrolysates over a wide molecular weight range (*m/z* 50–600).

For pyrolytic oils, other ways of sample pre-treatment like solid phase (micro) extraction (SPE and SPME) procedures may be used. The large variation in sample composition may lead to less reliable results. The SPE techniques for pyrolytic oils are now studied by Meier and co-workers [1]. An automated SPE technique for pyrolytic oils may be the extracting syringe, developed by Norberg and Thordarson [12].

Recently, Fullana [13] applied multidimensional GC–TOF-MS to pyrolytic oils to demonstrate the advantages of comprehensive 2D-GC. Group-type analysis was applied and an increased peak identification capacity of a factor of 1.5 in relation to normal GC–TOF-MS was mentioned. Another group-type analysis of oxygenated compounds in petroleum samples by comprehensive two-dimensional supercritical fluid chromatography and gas chromatography (SFC × GC) was published by Venter et al. [14]. By using a porous layer open tubular (PLOT) silica gel column good separation results were obtained for the non-polar compounds (alkanes and polyaromatic hydrocarbons) and the polar oxygenated fractions (ethers and alcohols). However, such silica (PLOT) columns are not likely to be applicable for water containing samples (e.g. pyrolysis oil) because of their unpredictable behaviour of retention time due to water interference.

Comprehensive 2D-GC-FID analysis of pyrolysis oil and HDO oils was published by Marsman et al. [15]. This paper also describes the first approach to classify the various components. The group-type classification of analytes in the oil samples proved to be a convenient method to get insights in the molecular composition of crude pyrolysis oil and hydrotreated oils. However, only a fraction of the chromatographable compounds has been identified so far by 2D-GC.

Dallüge et al. [16] published a review of several applications of GC × GC and group-type analysis. Modern time-of-flight mass spectrometers are able to generate some 5000 full scans/s (*m/z* 5–1000). By combination of a 2D-GC analysis with a fast scanning time-of-flight mass spectrometer (spectrum storage rate of 10–500 Hz), the separation capacity and identification quality of complex mixtures can be improved dramatically as shown and clearly explained by Vreuls et al. [17]. With their instrumental set up absolute detection and identification limits varying from 2 to 60 pg for pesticide analytes and 1 to 6 pg for poly aromatic hydrocarbons (PAHs) were obtained. The detector linearity range during ion trace analysis (extracted ion) showed to be 3 decades; i.e. 2 pg to 1 ng of their analytes. The MS detector response of individual components, however, is less uniform and may vary roughly a decade per mass quantity. This fact is less convenient for quantification purposes, because each individual component needs to be calibrated.

For the quality of identification of an analyte the similarity or the probability factor of a mass spectrum, as defined by Stein [18] can be used. The similarity parameter as used in this paper is defined in arbitrary units from 1 (low) to 1000 (high) and provides a value for the reliability of correct identification for each analyte.

In present study, comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (2D-GC–TOF-MS) is applied for identification and group- type classification of analytes in pyrolysis and HDO oils. The potential of the technique for the identification of compounds will be demonstrated. The gas chromatographic split injection temperature was varied (200–300 °C) to test the representativity of the sample. In this way the stability and reactivity of the analytes, during hot injection, was verified. A column screening of both, the first and second dimension was evaluated to optimize the chromatographic resolution.

Finally, a simple approach to classify the identified components of major concentration in the oil samples will be provided. Classification is performed by dividing the components into 9 chemical groups, describing approximately 75% of all chromatographic analytes. The hit quality of a specific functional analyte within a classification-group was verified by extractive ion detection of the spectral data. The relative results of the composition of a pyrolyis oil and its converted HDO oil will be compared.

## 2. Experimental

### 2.1. Sample preparation

The crude flash pyrolysis oil was produced from beech flakes using rotating cone technology and was obtained from BTG, Enschede, The Netherlands. The HDO oils were produced at the University of Groningen by treatment of the flash pyrolysis oil with hydrogen on a solid catalyst at 25 MPa and 573 K. Two heterogeneous catalysts were applied (Pd and Ru on carbon). After reaction, the apolar HDO oil was separated from the water layer by decantation. The formed water fraction is approximately 35 weight% of the initial pyroylis sample. Oil samples were stored at low temperature (<5 °C). Sample pre-treatment procedures were not performed. Before analysis, the oil sample was shaken vigorously and diluted with tetrahydrofuran (THF) (1:1, w/w). 0.1 μl of this homogeneous solution was injected in the split injector of the GC system (split ratio 1:10). Cleaning of the injection liner was necessary after approximately 20 injections.

Some relevant properties of the oils are shown in Table 1.

### 2.2. Instrumental settings

The analytical system used was a HP 6890N GC with auto-injector HP 7683 (Agilent Technologies, Palo Alto, CA, USA) connected to a Pegasus III time-of-flight mass spectrometer from LECO Instruments, St. Joseph, MI, USA. The TOF-MS oper-

Table 1
Some properties of the pyrolysis and HDO oil samples

| Composition/parameter | Dimension | Pyrolysis oil | HDO oil |
|---|---|---|---|
| Water by Karl Fischer | %w/w | 25 | <1 |
| pH | – | 3 | 3.5 |
| VOLATILE fraction (200 °C, 2 h) | %w/w | 68 | 77 |
| High molecular mass lignin (HMM) | %w/w | 8 | 8 |

ated at an acquisition rate of 100 spectra/s and a mass range of *m/z* 50–500 Da. Cryofocusing by liquid nitrogen and a quad jet modulator (Zoex, Houston, TX, USA) was applied. The modulation time was 10 s. Instrument control, data acquisition and processing were done by the ChromaTOF (LECO) software.

The first dimensional chromatographic separation was performed by an apolar column VF-5MS (5% phenyl in polydimethylsilicone; PDMS); 30 m; I.D. 0.25 mm, d.f. = 0.25 μm. The second dimensional column was situated in a dual internal oven and consisted of a phenyl (50%) PDMS column VF-17MS; 2 m; I.D. 0.1 mm, d.f. = 0.2 μm, both from Varian (Middelburg, The Netherlands). Temperature programming was performed at a starting temperature of 40 °C of the GC oven during 5 min and a rate of 3 °C/min to a final temperature of 330 °C. The dual column was programmed 10 °C ahead of the GC oven gradient. The carrier gas (helium 99.999%) flow rate was 1 $cm^3$/min; split injection of 0.1 μl sample solution at a split ratio of 1:10 and an injection temperature of 275 °C.

### 2.3. Data acquisition, identification and classification

The net $^2$D-retention time of n-decane (~0.6 s) was used as a reference. After loading of each chromatographic data file in the worksheet the $^2$D-retention time of decane was set to 0.600 s. In this way repeatable results were obtained under constant and stable instrumental conditions. Identification by the apex peakfinder algorithm and mass spectral deconvolution of the identified component was applied to integrate the peak area of the most abundant (selective) trace-ion signal by the ChromaTOF software. The deconvoluted spectra were compared within the NIST software library for correct matching. Group-type classification of components was also performed by the facilities of the software to draw border-lines in the contour plots. For calculation of the relative composition and the selection procedures for the main components (see text Section 3.1) the TOF-MS data files were transferred to Microsoft Excel.

## 3. Results and discussion

### 3.1. Column choice, chromatographic results and approach for classification of peaks

A typical flash pyrolysis oil, derived from beech wood, and two HDO oils (catalyst: Pd on carbon and Ru on carbon) were analysed by the GC × GC–TOF-MS system. The contour plots of the pyrolysis oil and a HDO sample are shown in Figs. 1 and 2, respectively.

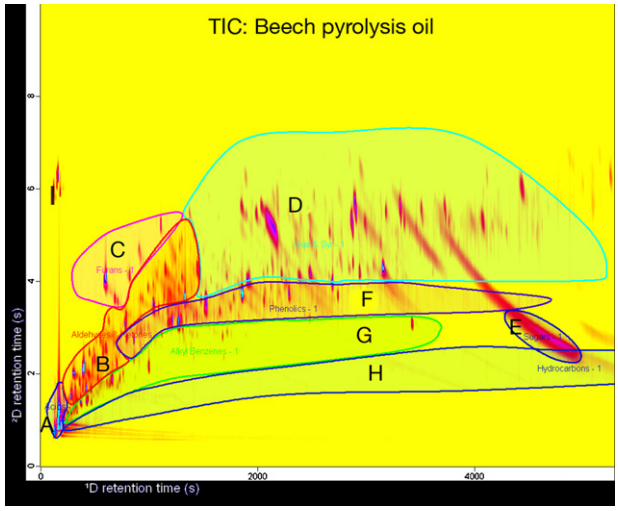


Fig. 1. Contour plot of the beech pyrolysis oil with group retention time fields A to H (see Section 3.1 and experimental conditions Section 2).

The chromatographic resolution of the analytes is high and the components are widely spread over the contour plot. Some peaks show front tailing behaviour, especially 1,6-anhydro-β-D-glucopyranose (levoglucosan) in the pyrolysis oil, due to its high concentration. Other column configurations were tested as well, but the results were not considerably better (see Section 2.2).

One attempt to increase the retention capacity of the very volatile co-eluting components (e.g. the continuous elution fraction of cyclopropanes, pentenes and volatile esters at $^1t_r$ = 130–160 s; $^2t_r$ = 1–10 s) by increasing the film thickness of the first column to 1 μm was successful, but resulted in less resolution of high boiling point components in the second dimension. This is due to the higher elution temperature of the first column, hence 2D retention times are dramatically reduced. For the selection of the second column a comparison was made for a phenyl/PDMS 50:50 phase (BPX-50; SGE, Australia), a cyanopropyl/PDMS 14:86 phase (Rtx 1701; Restek, USA)

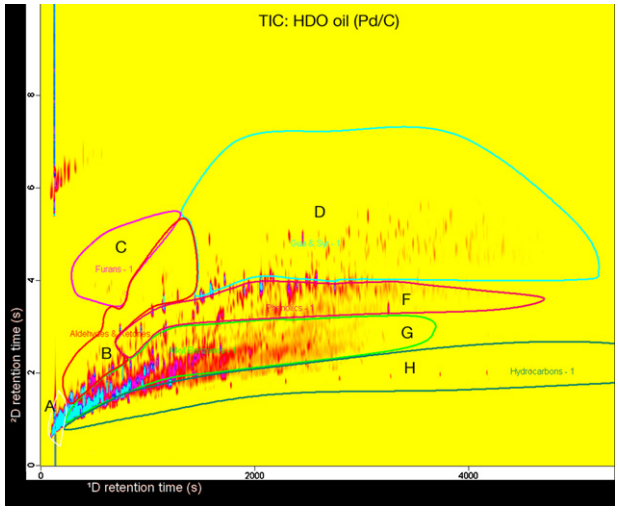


Fig. 2. Contour plot of the HDO oil (Pd catalyst on carbon) with group retention time fields A to H (see Section 3.1 and experimental conditions Section 2).

and a trifluoropropyl-methylpolysiloxane phase (VF200; Varian, The Netherlands), all of the dimension $L = 1$ m; I.D. 0.1 mm; $d_f = 0.1$ μm. The individual columns were tested both with a test mixture (alcohol, phenol and methoxyphenols) and by injection of a HDO sample. The elution order of the test components was essential similar. The overall chromatographic resolution of components in the HDO sample was also very similar for the three test columns in a 2D-GC-FID configuration. Thus, it may be concluded that the choice of the first column (apolar; boiling point separation) and its film thickness is of prime importance and that the second column should be polar. Sample injection temperature was examined by variation of the inlet temperature from 200 to 300 °C. As a result no significant modification of the chromatograms by GC–MS analysis was observed. The injection temperature was set for 275 °C for the current application.

The analytes in the contour plots (Figs. 1 and 2) are divided into 9 different groups. The borders of the groups were determined empirically by evaluation of the $^1$D-$^2$D retention time of identified components and by extractive (multiple) ion detection. However, it was experienced that selective ions were difficult to find within the group of components, especially for analytes with molecular masses below 120 Da. Once established, the borders were verified and corrected for both oils by applying selected detection again of several masses specific for the group. In this way an optimal collection of identical functional analytes was realized. The available software of the time-of-flight MS system allowed a precise limitation of the borders. The final classification template was applied to all samples. This results in 9 groups of retention time fields coded: A = acids; B = aldehydes and ketones; C = furans; D = guaiacols and syringols; E = sugars; F = phenolics; G = alkylbenzenes; H = hydrocarbons; I = residue, not classified. Group I contains all outsiders which do not belong to the specified groups (A to H). Examples are the fast $^1$D eluting components at $^1t_r = 130$–$160$ s; $^2t_r = 1$–$10$ s which consist of cyclopropanes, volatile formic esters and pentenes. This co-eluting fraction from the first column is not trapped by the cryogenic modulator. The complexity of the samples can be seen from the contour plots. Table 2 shows an overview of the number of detected peaks.

### 3.2. Fractionation of the oils

Hexane extraction (1:1, v/v) of the pyrolysis oil and a HDO oil was also applied to gain more insights in the composition of the oils. The fractions were analysed by 2D-GC-FID and GC–MS. Highly volatile components were not present in the samples and were presumably evaporated during the fractionation process. In Fig. 3 the partitioning of the components over the hexane extract (hexane solubles) and residue (hexane insolubles) is given. The apolar components (hydrocarbons) accumulate in the hexane phase while the sugars are present in the residue. Sugar components were not detected in the HDO oils.

For both pyrolysis and HDO oils, the phenolic components are distributed over both liquid phases. To get an impression of the partitioning of some phenolic compounds over both phases, the concentration ratio of two representative components in the hexane fraction and residue were determined. The concentration ratio of 4-methyl-2-methoxyphenol was determined as 1:2 and for the total phenolic fraction a ratio of 2:3 was found. For reasons of losses of volatiles, possible side reactions of components with the extraction solvents and to prevent laborious classical procedures, a direct injection of the oils in a chromatographic system will be clearly advantageous and lead to more representative, reliable and faster results.

### 3.3. Identification of the major components in the oil samples

To find out the main components in the oil samples a selection procedure was defined. First of all the absolute peak areas of the solvent peak, its inhibitor (butylated hydroxytoluene) and the internal standard (*n*-decane) were removed. Next, the residual peak areas of the remaining peaks were converted to their relative area contribution (100%). The first selection of analytes was performed by setting a minimum relative peak area >0.5%. This results in the main composition of the oil samples (Table 3). A universal detector response was assumed. This is not a valid procedure to determine the absolute concentrations. However, it allows determination of the relative concentration of the individual analytes and thus can be used to compare concentrations of various components in the oils under study.

Integration of peak area of the analyte by identical trace ion was verified for each sample. In this way each component in each sample is detected by the same detector response, making comparison between the oil samples most representative. For the pyrolysis oil sample 23 individual analytes were selected, describing 58% of the total area composition. For the HDO oils 31 identified peaks (25% of relative area) and 31 (30% of relative area) of the palladium and ruthenium catalyst were found, respectively. By this procedure the differences of the main chem-

Table 2
Summary of the number of peaks detected in the oil samples[a]

| Criteria for selection[b] | Number of peaks detected (*n*) and their relative area: (between brackets: %) | | |
|---|---|---|---|
| | (*n*) Beech (%) | (*n*) HDO (Pd) (%) | (*n*) HDO (Ru) (%) |
| 1. Total number of peaks | 810 (100) | 2385 (100) | 1925 (100) |
| 2. Peak area >0.5% | 23 (58) | 31 (25) | 31 (30) |
| 3. Peak area >0.3% | 338 (94) | 546 (84) | 600 (85) |
| 4. Peak area >0.3% + similarity >850 and peak area >0.1% | 248 (88) | 373 (74) | 368 (73) |

[a] For 2D-GC–TOF-MS conditions: see exp. Section 2.
[b] Selection criteria: see Section 3.2.

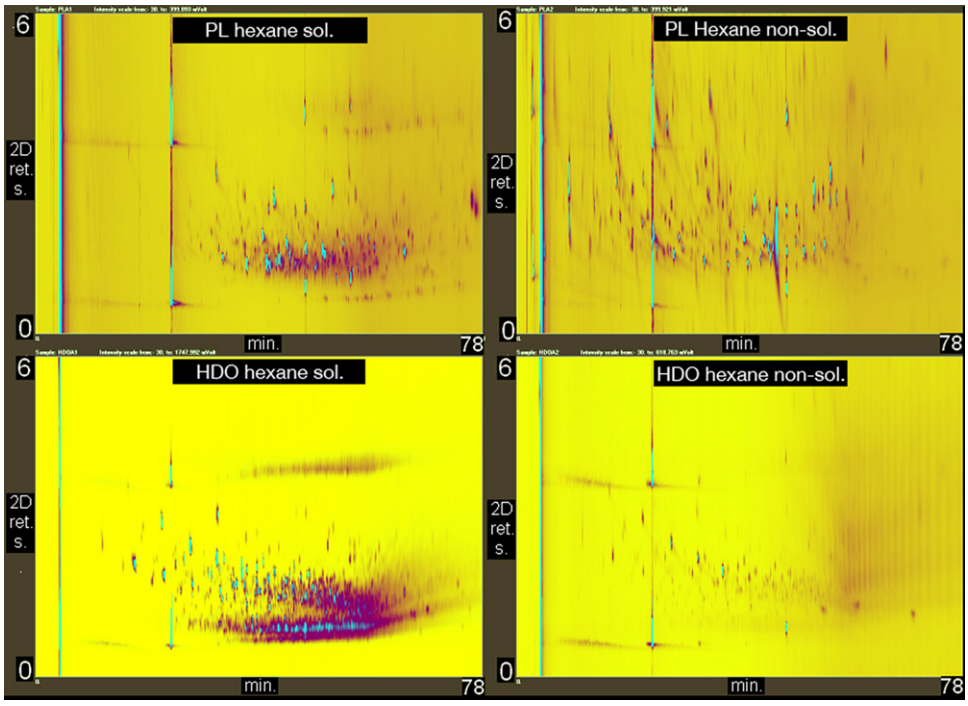


Fig. 3. Contour plots of the hexane solubles and hexane non-solubles after hexane extraction of a pyrolysis oil and its converted HDO oil by 2D-GC-FID.

ical structures of the composition of flash pyrolysis oil and the HDO oils can be listed immediately. Levoglucosan, aldehydes and ketones from sugar derivatives (furaldehyde, furanone) and guaiacols (methoxyphenols) are present in the crude pyrolysis oil. The HDO oils are rich in alkane isomers and alkylated benzenes. Examples are isomers of cyclopentane, cyclopentene, cyclohexane and dimethylbenzene, as can be seen in Table 3.

### 3.4. Classification and further selection criteria

For the interpretation studies of molecular structure modifications in the pyrolytic oils, it is important to rely on correct incorporation of the chemical functional analytes within a group. An approach was made to examine the correctness of classification for the numerous (co eluting) analytes in contour plots.

As described in Section 3.1, nine different groups of organic components (A–I) were defined. It is assumed that all target components within a certain retention time field belong to this group of homologue components. This is not completely correct because some homologues elute in neighbouring retention time fields. Examination of the correctness of classification for each component is very laborious due to the large amount of analytes. If only components >0.5% will be examined the representativity of the samples is too low (25–58%, see Section 3.3). So a new selection was made. By selection of components with relative area >0.3% and better identification similarity >850 (the latter restricted by the condition of only relative areas below 0.1%) some 250–375 well identified analytes remain. This total selection now represents approximately 75% of the total relative sample area.

From Table 2, selection 4 it can be seen that the number of analytes decreased considerably.

To be sure that a classification group contains most of its target compounds, the correctness of the classification was determined. All listed components >0.3% relative area within the classification group were individually verified for the correct functionality. The conditions for positive hits are: A: analyte with carboxylic group; B: components with C=O; C: cyclic oxygen containing component; D: all methoxy-phenolic derivatives; E: all glycosides as derivatives of glucose (intra molecular anhydrides); F: hydroxy-benzene derivatives excluding methoxy-phenols; G: alkyl substituted benzenes; H: aliphatic and cyclic hydrocarbons. For example if a methoxy-phenol was found in group D (guaiacols and seringols) it is qualified as a correct hit, while a phenolic component in group G (alkyl benzenes) is qualified as a false hit, etc. The percentage of correct hits related to the total number of analytes in the group was defined as the correctness of qualification. High correctness (50–90%) was observed for the most dominant groups in the samples. The correctness percentage of classification (see Table 4) may serve as an indicator for the homogeneity of the major homologue components in a group. The data are valuable to indicate the reliability of group classification of components, hence for correct interpretation of changes in the molecular structure distribution of the samples. Especially, when the TOF-MS method will be transferred to a 2D-GC-FID application, the reliability of group classification is an important aspect.

### 3.5. Comparison of the composition of pyrolysis oil and HDO oils based on total relative peak area of the classified groups A–I

The classified group approach (see Section 3.1) was applied to the contour plots of all samples. Subsequently, the total rel-

Table 3
List of main components (>0.5% relative area contribution) in the pyrolyis and HDO oils[a]

| Main components (>0.5% relative area) | CAS no. | Beech, %area | PdC, %area | Ru 8, %area |
|---|---|---|---|---|
| *N*-Methyl-D-glucamine (Meglumine) | 6284-40-8 | 1.7 | | |
| Propanoic acid, ethyl ester | 105-37-3 | 0.6 | | |
| 1-Hydroxy-2-butanone | 5077-67-8 | 1.2 | | |
| Butanedial | 638-37-9 | 1.7 | | |
| 2-Cyclopenten-1-one | 930-30-3 | 0.5 | | |
| 3-Furaldehyde | 498-60-2 | 2.9 | | |
| Ethane, 1-ethoxy-1-methoxy- | 10471-14-4 | 1.0 | | |
| 2(5H)-Furanone | 497-23-4 | 3.2 | | |
| 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- | 80-71-7 | 0.6 | | |
| 4-Methyl-5H-furan-2-one | 6124-79-4 | 0.6 | | |
| Propyl nitrite | 543-67-9 | 0.5 | | |
| 2,2-Dimethyl-3-heptanone | 19078-97-8 | 0.6 | | |
| 4-methoxyphenol (Mequinol) | 150-76-5 | 1.8 | | |
| 6-Hepten-2-one, 5,7,7-trichloro- | 0-00-0 | 0.7 | | |
| Acetic acid, trimethylsilyl ester | 18147-36-9 | 0.8 | | |
| Phenol, 2-methoxy-4-methyl- | 93-51-6 | 1.4 | | |
| 1,2-Benzenediol | 120-80-9 | 1.1 | | |
| 2-Furancarboxaldehyde, 5-(hydroxymethyl)- | 67-47-0 | 3.5 | | |
| 1-Propene, 3-methoxy-2-methyl- | 22418-49-1 | 0.9 | | |
| 3-Hydroxy-4-methoxymandelic acid | 3695-24-7 | 0.6 | | |
| Phenol, 2-methoxy-4-(1-propenyl)- | 97-54-1 | 0.6 | | |
| 1,6-Anhydro-á-D-glucopyranose (levoglucosan) | 498-07-7 | 23.9 | | |
| Propanal, 2,2-dimethyl- | 630-19-3 | | 0.7 | |
| Cyclopropane, 1,2,3-trimethyl- | 42984-19-0 | | 0.7 | |
| Cyclohexane | 110-82-7 | | | 0.6 |
| Cyclopentane, ethyl- | 1640-89-7 | | 0.8 | 1.2 |
| 3-Pentanone, 2-methyl- | 565-69-5 | | 0.7 | 1.0 |
| Pentane, 2,2,3,3-tetramethyl- | 7154-79-2 | | 0.7 | |
| Butanoic acid | 107-92-6 | | 0.8 | 2.6 |
| 4-Methyl-1,3-heptadiene (c,t) | 17603-57-5 | | 0.6 | |
| 1-Ethyl-2-(4-methylpentyl)cyclopentane | 219726-60-0 | | 0.6 | |
| Cyclopentane, propyl- | 2040-96-2 | | 0.7 | |
| Cyclohexene, 3-methyl- | 591-48-0 | | | 0.7 |
| Cyclopentane, 1-ethyl-3-methyl-, *cis*- | 2613-66-3 | | | 1.1 |
| 1-Ethyl-5-methylcyclopentene | 97797-57-4 | | 0.7 | 0.8 |
| Cyclopentene, 1-propyl- | 3074-61-1 | | 0.7 | 0.9 |
| Cyclohexene, 3-ethyl- | 2808-71-1 | | 0.8 | 0.9 |
| Cyclohexene, 3-methyl- | 591-48-0 | | | 0.7 |
| Cyclopentane, 1-ethyl-3-methyl-, cis- | 2613-66-3 | | | 1.1 |
| Cyclopentene, 1-ethyl-5-methyl- | 97797-57-4 | | | 0.8 |
| Decane, 2,5-dimethyl- | 17312-50-4 | | 0.6 | |
| Benzene, dimethyl- | 108-38-3 | | 0.8 | 0.5 |
| Ethylbenzene | 100-41-4 | | | 1.0 |
| trans-1,3-Diethylcyclopentane | 0-00-0 | | 0.7 | |
| Nonane | 111-84-2 | | 0.5 | |
| Propanedioic acid, propyl- | 616-62-6 | | 2.7 | |
| 4,4-Dimethyl-oct-5-enal | 0-00-0 | | 1.2 | |
| Cyclopentane, 1-methyl-2-propyl- | 3728-57-2 | | 0.7 | |
| 1-Cyclobutanone, 2-(2-methyl-1-propenyl) | 91531-45-2 | | 0.8 | |
| Pentalene, octahydro-1-methyl- | 32273-77-1 | | 0.9 | |
| Cyclohexene,1-propyl- | 2539-75-5 | | 0.6 | 1.0 |
| Cyclohexane, ethyl- | 1678-91-7 | | | 1.6 |
| 3-Hexanone, 4-methyl- | 17042-16-9 | | | 1.0 |
| Benzene, 1-ethyl-2-methyl- | 611-14-3 | | 0.7 | |
| Cyclooctane, methyl- | 1502-38-1 | | 0.9 | |
| Phenol | 108-95-2 | | 0.5 | 1.3 |
| Phenol, 3-methyl- | 108-39-4 | | 0.5 | 1.1 |
| Phenol, ethyl- | 123-07-9 | | 0.6 | 1.6 |
| Phenol, ethyl-methyl- | 1687-64-5 | | 0.5 | 1.1 |
| Phenol, propyl- | 645-56-7 | | 0.5 | 0.7 |
| 2-Methyl-6-propylphenol | 3520-52-3 | | 0.6 | 0.5 |
| Pentanoic acid | 109-52-4 | | | 2.2 |

Table 3 (*Continued*)

| Main components (>0.5% relative area) | CAS no. | Beech, %area | PdC, %area | Ru 8, %area |
|---|---|---|---|---|
| Cyclohexane, 1-ethyl-4-methyl-, *trans*- | 6236-88-0 | | | 0.6 |
| Cyclononene | 9-11-3618 | | | 0.9 |
| Benzene, propyl- | 103-65-1 | | | 0.5 |
| Phenol, 2,3-dimethyl- | 526-75-0 | | | 0.8 |
| 4-*n*-Propylbenzoic acid | 3-5-2438 | | | 0.5 |
| Unknown | | 7.5 | 3.2 | 2.7 |
| Sum of main components | | 58.0 | 25.5 | 29.5 |

Beech = crude flash pyrolysis oil; HDO(Pd) = converted oil by palladium catalyst; HDO(Ru8) = converted oil by ruthenium catalyst.
[a] Identified name of component, chemical abstract service CAS number and its relative contribution to the sample.

ative peak area of each group was calculated. In this way the total chromatographable fraction of the oil sample is classified in the nine groups A–I. The results for pyrolysis oil and HDO oil can be compared and give insights in the reactivity of the various components of pyrolysis oil during the hydrodeoxygenation process. The relative data are shown in a histogram in Fig. 4.

It can be seen that hydrotreating leads to complete sugar conversion. The amounts of aldehydes, ketones and furans are also decreasing considerably. Significant amounts of hydrocarbons (alkylbenzenes and aliphatic hydrocarbons) are formed. The HDO oils produced by the palladium catalyst are enriched in alkylbenzenes, while the ruthenium catalyst gives a higher proportion of aliphatic hydrocarbons.

Acids are hardly converted upon hydrodeoxygenation. However, the fast eluting acid fraction in the contour plot (see Figs. 2 and 3) contains several volatile esters of acetic- and

Table 4
Results of correctness of classification for components in group A–I[a]

| | Group of classification[a], *n* = number of peaks[b], correctness = number of hits[c] | Pyrolysis oil Beech | HDO-Pd/C | HDO-Ru8/C |
|---|---|---|---|---|
| | Acids (%) | 8.3 | 7.8 | 7.0 |
| A | *n* | 15 | 28 | 18 |
| | Correctness | 7 (47%)[d] | 8 (28%) | 3 (17%) |
| | Aldehydes and ketones (%) | 18.7 | 10.0 | 4.2 |
| B | *n* | 54 | 29 | 12 |
| | Correctness | 28 (52%) | 4(14%) | 8(67%) |
| | Furans (%) | 5.3 | 0.3 | 0.2 |
| C | *n* | 9 | 7 | 4 |
| | Correctness | 7(78%) | 5(71%) | 3(75%) |
| | Guaiacols and syringols (%) | 19.7 | 4.0 | 1.9 |
| D | *n* | 66 | 28 | 25 |
| | Correctness | 45(68%) | 3(11%) | 6(24%) |
| | Sugar (%) | 21.4 | 0 | 0 |
| E | *n* | 16 | – | – |
| | Correctness | 16(100%) | – | – |
| | Phenolics (%) | 7.4 | 9.2 | 15.0 |
| F | *n* | 22 | 61 | 71 |
| | Correctness | 9(41%) | 44(72%) | 48(68%) |
| | Alkylbenzenes (%) | 1.8 | 29.5 | 24.7 |
| G | *n* | 10 | 131 | 117 |
| | Correctness | 3(30%) | 96(73%) | 55(47%) |
| | Hydrocarbons (%) | 0.4 | 3.3 | 10.9 |
| H | *n* | 6 | 26 | 62 |
| | Correctness | 0(0%) | 22(85%) | 57(92%) |
| | Not classified (%) | 5.3 | 9.9 | 9.5 |
| I | *n* | 26 | 46 | 45 |
| | Correctness | – | – | – |
| | Total area of composition (%) | 88 | 74 | 73 |
| | Total number of peaks (*n*) | 224 | 356 | 354 |

[a] First line points out the total relative area of components >0.3% in the specified group.
[b] Second line *n* = the number of components in the specified group.
[c] Third line indicates the number of correct hits belonging to the specified group.
[d] Between brackets its percentage (see also selection criteria from Table 1).

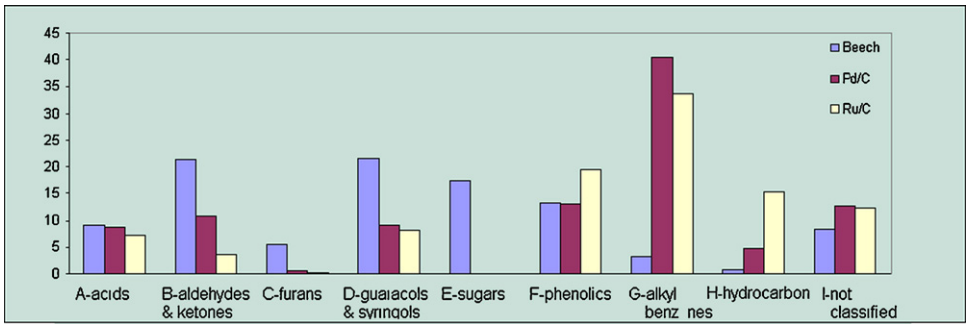


Fig. 4. Histogram for comparison of the oil compositions based on total relative peak area of the classification groups (A–I).

formic acid and aldehydes (detected by TOF-MS). The inhomogeneity of the acid group is also indicated by its low correctness of classification (47% for pyrolysis oil and 22% for HDO oil, see Table 4). Group I (un-classified analytes) shows a minimal increase upon hydrotreatment. This is due to the very volatile fraction of components at $^{1}t_r = 130–160$ s; $^{2}t_r = 1–10$ s) which consist of cyclopropanes, volatile formic esters and pentenes, not present in the pyrolysis oil. The newly detected hydroxy-naphtalenes in the HDO oil samples ($^{1}t_r = 2500–3800$ s; $^{2}t_r = 3–4.5$ s) also contribute to group I.

Thus, by proper evaluation of 2D-GC-TOF-MS data before and after hydrotreating, valuable information on the molecular processes taking place during the HDO reaction may be obtained. This will lead to a better understanding of the HDO process and will aid the development of highly efficient catalysts.

Finally, it can be stated that all obtained information by the 2D-GC-TOF-MS technique is not only useful for the chemical study as such, but also provides the basic knowledge for method transfer to a 2D-GC-FID application. The advantages of a routinely FID application are the economical costs and the ease of calibration due to its universal detection response, making absolute quantification of samples much more convenient.

## 4. Conclusions

The technique of 2D-GC–TOF-MS is a very powerful tool to identify individual components in fast-pyrolysis oil and hydrotreated samples thereof. A total of about 1000 and 2000 analytes were detected in the crude pyrolysis oil and the HDO oil, respectively. By simple software handling a reduction of the chromatographic and mass spectral data was obtained to describe 75% of the sample composition by approximately 350 analytes.

Several of these components were not detected before in pyrolysis oils and derivatives (e.g. isomers of tetrahydronaphtalenes). The major component classes (analytes >0.5% relative area) in the pyrolysis oils are aldehydes, esters of organic acids and mono- and dimethoxy phenols (guaiacolic- and seringolic derivatives), while significant amounts of cyclic hydrocarbons and alkylated phenolic derivatives are present in the HDO oil.

Classification of homologue analytes could be optimized by application of the known $^{1}D/^{2}D$ retention times of the identified components. The corrections of the borders of retention time fields resulted in more precision of the group contours related to a 2D-GC-FID application with model components from earlier studies. Analytes within a group were verified for their correctness of classification. The value of correctness, i.e. the percentage of correct hits in the group, was a function of the nature of the oil. High correctness (50–90%) was observed for the most dominant groups in a sample, confirming the reliability of grouping.

Absolute quantification of the concentrations of individual components in the oils is less reliable due to the unknown mass detector response of individual components. A 2D-GC-FID application will be more convenient for absolute quantification.

However, the relative composition of the oils may be obtained by summation of the relative areas of groups of analytes. In this way, determination of the relative change in molecular composition between the various oils is possible. With this approach, it can be shown that the amounts of apolar alkylated benzenes and hydrocarbons strongly increase by hydrotreating of pyrolysis oil. 2D-GC–TOF-MS thus allows us to obtain rapid and reliable insights in the molecular processes taking place during the hydrodeoxygenation process. This will be very beneficial for future exploratory catalyst screening and process research and development activities on the HDO process.

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